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Technical Report No. 3

"Reactions of Carbon Disulfide and Carbon Dioxide Adducts
$(\eta^5\text{-}C_5H_5)(CO)_2\text{Fe-CX}_2^-$ with Organoiron Electrophiles"

by

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Prepared for Publication

in the

Journal of Organometallic Chemistry

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Troy, New York 12180

September 25, 1988

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION		1b. RESTRICTIVE MARKINGS
UNCLASSIFIED		
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT
		APPROVED FOR PUBLIC RELEASE:
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE		DISTRIBUTION UNLIMITED

4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
NO. 3	N00014-87 K 0465

6a. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
ALAN CUTLER RENSSELAER POLYTECHNIC INSTITUTE		OFFICE OF NAVAL RESEARCH DR. HAROLD GUARD

6c. ADDRESS (City, State, and ZIP Code)	7b. ADDRESS (City, State, and ZIP Code)
DEPARTMENT OF CHEMISTRY TROY, N.Y. 12180	CODE 1113 800 N. QUINCY STREET ARLINGTON, VA 22217

8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
ONR	413	

8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS			
	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO
(see 7b)				

11. TITLE (Include Security Classification)

Reactions of Carbon Disulfide and Carbon Dioxide Adducts $(\eta-C_5H_5)(CO)_2Fe-CX_2^-$ with Organoiron Electrophiles

12. PERSONAL AUTHOR(S)
Mary E. Giuseppetti, Bruce E. Landrum, John L. Shibley, and Alan R. Cutler

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
TECHNICAL	FROM _____ TO _____	October 3, 1988	

16. SUPPLEMENTARY NOTATION

Submitted for publication in "Journal of Organometallic Chemistry"

17.	COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Reactions of Fp-$CS_2^-K^+$ (2) and Fp-$CO_2^-Na^+$ (and Li⁺) (1) [Fp=$(\eta^5-C_5H_5)(CO)_2$Fe] with organoiron electrophiles FpX (X=I, OSO_2CF_3, HgCl), $(\eta^5-C_5H_5)L(CO)$FeI [L=P(OPh)₃, PPh₃], and $(\eta^5-C_5H_5)(CO)$Fe$(CH_3CN)_2^+ PF_6^-$ are contrasted. Treatment of the CS_2 adduct 2 with the bis-acetonitrile salt gives the $\mu(\eta^1-C:\eta^2-S,S')$ CS_2 complex Fp-C(S)S-Fe(CO)Cp (4). Reacting the CO_2 adduct 5 with the iron electrophiles Cp(L)(CO)Fe-I affords Fp_2, with only trace amounts of Fp-Fe(CO)(L)Cp (for L=PPh₃ and P(OPh)₃) evident. No $\mu(\eta^1-C:\eta^1-O)$ bimetallocarboxylate intermediates Fp-C(O)O-Fe(L)(CO)Cp are detected. In contrast, Fp⁻Na⁺ upon treating with $(\eta^5-C_5H_5)L(CO)$FeI gives 1:1 mixtures of Fp_2 and Fp·Fe(CO)(L)Cp (for L=PPh₃ and P(OPh)₃). The bis-acetonitrile electrophile and 1 afford initially the mixed dimer Fp-Fe$(CH_3CN)(CO)$Cp, which degrades to Fp_2 at room temperature.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	UNCLASSIFIED
22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code) 22c. OFFICE SYMBOL

DD FORM 1473, 84 MAR   83 APR edition may be used until exhausted.   SECURITY CLASSIFICATION OF THIS PAGE
All other editions are obsolete.

Reactions of Carbon Disulfide and Carbon Dioxide Adducts

$(\eta\text{-}C_5H_5)(CO)_2Fe\text{-}CX_2^-$ with Organoiron Electrophiles

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Abstract

Reactions of $Fp\text{-}CS_2^-K^+$ (1) and $Fp\text{-}CO_2^-Na^+$ (and Li^+) (2) $[Fp=(\eta^5\text{-}C_5H_5)(CO)_2Fe]$ with organoiron electrophiles FpX (X=I, OSO_2CF_3, HgCl), $(\eta^5\text{-}C_5H_5)L(CO)FeI$ [L=P(OPh)$_3$, PPh$_3$], and $(\eta^5\text{-}C_5H_5)(CO)Fe(CH_3CN)_2^+ PF_6^-$ are contrasted. Treatment of the CS_2 adduct 2 with the bis-acetonitrile salt gives the $\mu(\eta^1\text{-}C:\eta^2\text{-}S,S')$ CS_2 complex $Fp\text{-}C(S)S\text{-}Fe(CO)Cp$ (4). Photolysis of the known $\mu(\eta^1\text{-}C:\eta^1\text{-}S)$ CS_2 compound $Fp\text{-}C(S)S\text{-}Fp$ (3) only generates traces of 3, in contrast. Reacting the CO_2 adduct 5 with the iron electrophiles $Cp(L)(CO)Fe\text{-}I$ affords Fp_2, with only trace amounts of $Fp\text{-}Fe(CO)(L)Cp$ (for L=PPh$_3$ and P(OPh)$_3$) evident. No $\mu(\eta^1\text{-}C:\eta^1\text{-}O)$ bimetallocarboxylate intermediates $Fp\text{-}C(O)O\text{-}Fe(L)(CO)Cp$ are detected. In contrast, Fp^-Na^+ upon treating with $(\eta^5\text{-}C_5H_5)L(CO)FeI$ gives 1:1 mixtures of Fp_2 and $Fp\text{-}Fe(CO)(L)Cp$ (for L=PPh$_3$ and P(OPh)$_3$). The bis-acetonitrile electrophile and 1 afford initially the mixed dimer $Fp\text{-}Fe(CH_3CN)(CO)Cp$, which degrades to Fp_2 at room temperature. Organic carboxylates $RCO_2^-M^+$ (R=Ph, CH_2Ph, and t-Bu; $M^+=Li^+$, Na^+, K^+) do not react with $(\eta^5\text{-}C_5H_5)(CO)Fe(CH_3CN)_2^+$; and photolysis of Fp(acetate) produces only Fp_2, not an $(\eta^2\text{-}O,O')$ acetate complex $(\eta^5\text{-}C_5H_5)(CO)FeO(O)CCH_3$.

Introduction

Availability of analogous pairs of carbon dioxide [1] and carbon disulfide [2] transition-metal complexes permits comparing structure-bonding and chemical reactivity of these ligated heterocumulenes [3]. Such comparisons permit us to address the prevalent but questionable attitude that studying the generally more accessible CS_2 adducts affords insight into their less stable (or more labile) CO_2 congeners [4]. We are interested in one pair of $(\eta^1\text{-C})$-bonded heterocumulene complexes, the $Fe(CO)_2Cp$ metallodithiocarboxylates $Fp\text{-}CS_2^-$ (Na^+, K^+) (1) [5] and metallocarboxylates $Fp\text{-}CO_2^-$ (Li^+, Na^+) (2) [6]. Although 1 and 2 are unstable at room temperature and have not been isolated as solids, they exhibit high reactivity in solution towards electrophiles [7].

The Fp(dithiocarboxylate) anion (1) in particular readily reacts with a variety of Lewis acids. Alkylation or silation of 1 at -20 °C gives stable dithiocarboxylate ester complexes (eq 1) [5,8]. Ellis [5] initially demonstrated that treating 1 with FpI affords the stable $\mu(\eta^1\text{-C}{:}\eta^1\text{-S})$

$$(1)$$
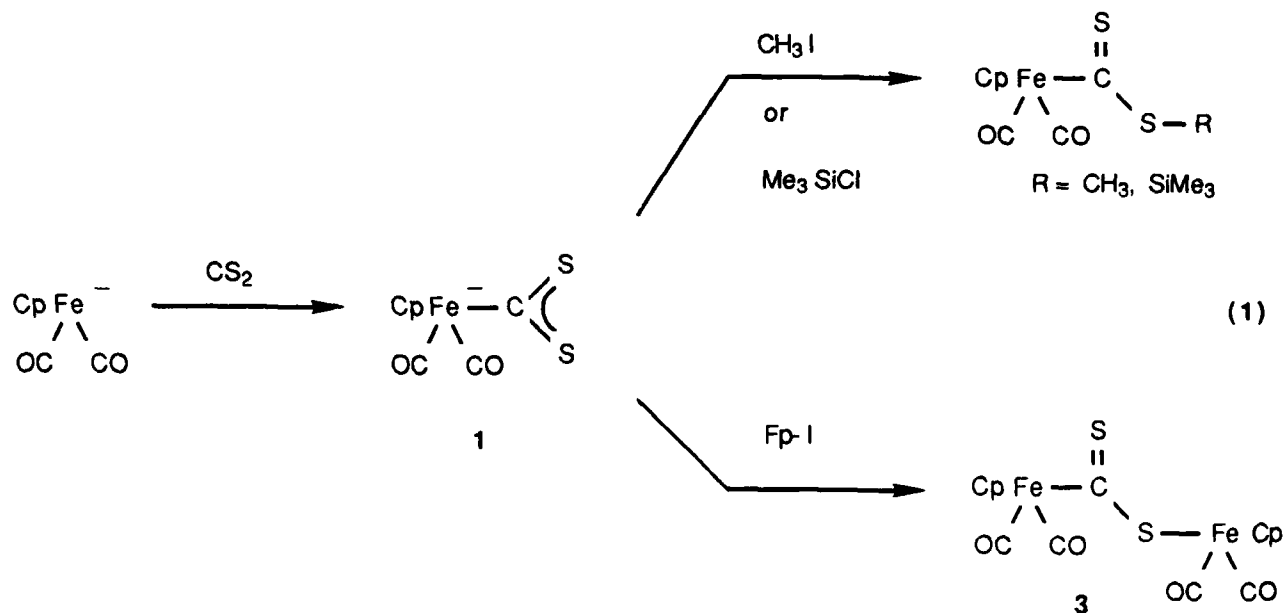
bis-Fp dithiocarboxylate 3 [8d,9c] in good yield. This $\mu\text{-}CS_2$ adduct further serves as a useful

precursor to trimetallic $\mu(\eta^1\text{-}C{:}\eta^1\text{-}S{:}\eta^1\text{-}S')$ CS_2 derivatives. For example, electrophilic organoiron reagents that generate Fp^+ convert 1 into $Fp\text{-}C(SFp)_2^+$ [9a]. These results appear general in that a variety of stable bimetallic and trimetallic $\mu\text{-}CS_2$ complexes derived from 1 have been characterized [9].
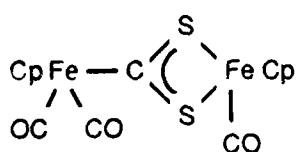
Reactions of the CO_2 complexes 2 with Lewis acids are more involved. Electrophilic methylating agents including methyl iodide and methyl triflate quantitatively convert 2 (Li^+,Na^+, or K^+) to $Fp\text{-}CH_3$ [6,10,11], a result that is consistent with these electrophiles intercepting a dissociative equilibrium between 2 and Fp^- (eq 2). Blocking this dissociation of 2 by using the
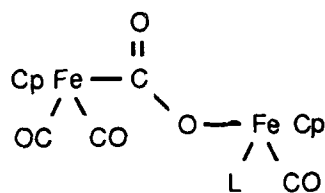

$$(2)$$
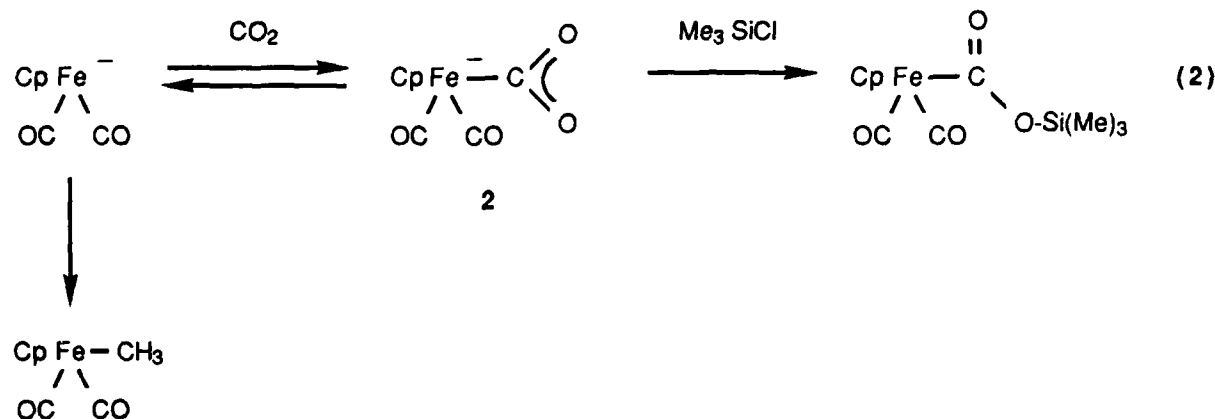
more oxophilic Mg^{+2} counterion, which evidently chelates 2 as a $\mu(\eta^1\text{-}C{:}\eta^2\text{-}O,O')$ metallo-carboxylate $[Fp\text{-}C(O)O]_2Mg$, expedites methylation of 2 to selectively give its metalloester $FpCO_2CH_3$ in good yield [10b]. As an alternative strategy, using oxophilic trialkylsilyl chlorides efficiently traps 2 (Li^+ or Na^+) as its silylesters $Fp\text{-}C(O)O\text{-}SiMe_2R$ ($R=CH_3$, t-Bu) [10e,12*] The extremely robust $Fp\text{-}SiMe_3$ is not detected in these reactions. Results of reacting 2 with transition organometallic Lewis acids have not been reported; indeed, few bimetallic $\mu\text{-}CO_2$ adducts have been prepared [13].

In this paper we compare the reactivity of 1 and 2 towards organoiron electrophiles. These electrophiles were selected so as to contain either one or two accessible coordination sites [14]; $Fp\text{-}X(X=I, OSO_2CF_3)$ and $Cp(CO)Fe(CH_3CN)_2^+BF_4^-$, respectively, are representative Lewis acids. Target molecules are the $\mu\text{-}CS_2$ complexes 3 [5] and 4 [9c] and the $\mu\text{-}CO_2$ metallocarboxylates 5 and 6.

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    *   Reference numbers with asterisks indicate notes in the list of references.
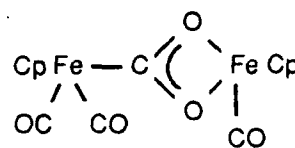
CpFe—C(S)(S)FeCp structure with OC CO and CO ligands

4

CpFe—C(=O)(O)—FeCp structure with OC CO and L CO ligands

5 (a) L = CO

(b) L = P(OPh$_3$)

(c) L = PPh$_3$

CpFe—C(O)(O)FeCp structure with OC CO and CO ligands

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Experimental Section

Synthetic manipulations were performed under a nitrogen atmosphere using standard syringe-septum and Schlenk techniques or a glovebox [15]. Infrared spectra were taken as CH_2Cl_2 or THF solutions or as pressed KBr disks and were recorded on a Perkin-Elmer Model 297 spectrophotometer. The $\nu(CO)$ frequencies (2200-1500 cm^{-1}) were calibrated against the polystyrene 1601 cm^{-1} absorption; they are accurate to ±2 cm^{-1} below and ±5 cm^{-1} above 2000 cm^{-1}. NMR spectral data were obtained on a Varian Model XL-200 or a Bruker Model WP-100 spectrometer; chemical shifts (δ) are referenced to internal $(CH_3)_4Si$. Combustion microanalysis were done by Robertson Laboratory, Inc., Madison, NJ.

Organic reagents were obtained commercially and used as received. Dichloromethane was distilled under nitrogen from P_2O_5; anhydrous THF and diethyl ether were distilled from sodium benzophenone ketyl. Organometallic starting materials Fp$_2$ [16], FpCH$_3$ [16], FpI [16], FpHgCl [17], Fp$^-$K$^+$ [18], Cp(CO)Fe(CH$_3$CN)$_2{}^+$PF$_6{}^-$ [19], Cp(PPh$_3$)(CO)FeI [20], and Cp[P(OPh)$_3$](CO)FeI [21] were prepared by literature procedures and judged pure by IR and ^{1}H NMR spectroscopy.

Preparation of Cp(CO)$_2$Fe-C(S)S-Fe(CO)$_2$Cp (3).

The procedure of Ellis and coworkers [5] was followed. A THF solution of Cp(CO)$_2$Fe$^-$Na$^+$ (11.0 mmol, 150 mL), prepared by Na(Hg) cleavage of Fp$_2$ (2.00 g), was cooled to -78 °C and treated with carbon disulfide (1.5 mL, 22.8 mmol). Cp(CO)$_2$FeI (3.40 g, 11.2 mmol) then was added to the resulting dark red solution containing Cp(CO)$_2$FeCS$_2{}^-$Na$^+$ (1), and the reaction

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solution was maintained at -78 °C (1 h). After warming (22 °C), the solution next was filtered through celite; the THF was evaporated; and the dark red powder was recrystallized twice from dichloromethane-heptane (-78 °C). Yield 4.58 g (97%) Fp-C(S)S-Fp (3); IR (THF) 2038, 2021, 1990(sh), 1979(br) cm^{-1} (CO); (CH$_2$Cl$_2$) 2040, 2025, 1994(sh), 1981(br) cm^{-1} (CO), 1005 cm^{-1} (CS); ^{1}H NMR (CDCl$_3$) δ 4.96 (CpFeS), 4.83 (CpFeC); ^{13}C NMR (CDCl$_3$) δ 298.2 (FeCS$_2$Fe), 214.0 and 212.6 (CO), 87.9 and 85.8 (Cp).

Preparation of Cp(CO)$_2$Fe-C(S̄)S̄-Fe(CO)Cp (4).

In a glove box, FpK (0.496 g, 2.30 mmol) was transferred to a 250-mL side-arm flask. After removing from the glovebox, the flask was cooled (-78 °C) before adding 100 mL of THF. The orange solution turned red-orange as carbon disulfide (0.28 mL, 2.53 mmol) was added dropwise by syringe. IR spectral monitoring of the cold, dark-red solution (5 min) indicated completed conversion to FpCS$_2^-$K$^+$ (1) [ν(CO) 1998, 1944 cm^{-1}] plus varying amounts of Fp$_2$ (2-10%). In separate experiments, warming this solution above -20 °C exclusively affords Fp$_2$; {^{1}H}^{13}C NMR spectra of 1-K$^+$ in THF (-78 °C): δ 308.9 (FeCS$_2$), 215.2 (CO), 88.0 (Cp).

The THF solution containing FpCS$_2^-$K$^+$ (2) was treated with Cp(CO)Fe(CH$_3$CN)$_2^+$PF$_6^-$ (0.950 g, 2.53 mmol) and maintained at -78 °C (0.5 h). The resulting red-orange solution was warmed to room temperature before evaporating the solvent under reduced pressure and exhaustively extracting the residue with benzene (5x6 mL). Benzene was evaporated from the combined filtrates, and the resulting red solid was extracted with hexane. Flash column chromatography (silica gel, 4.5x15 cm column) of the combined red hexane extracts was used to separate the reaction mixture. Elution with 2% ethyl acetate in hexane removed faint yellow and brown bands; these afforded very small amounts of an unidentified material and Fp$_2$, respectively. A final red band was eluted using 4-6% ethyl acetate in hexane; removal of solvent left 0.291 g of a red powder that was identified as Fp-C(S̄)S̄-Fe(CO)Cp (4) [9c] (31%): IR (CH$_2$Cl$_2$) 2025, 1989, 1938(br) cm-1 (CO); IR (KBr) 2028, 1980, 1913(br) (CO), 914, 875 cm^{-1} (CS$_2$); 1H NMR (CDCl$_3$) δ 4.85 (Cp, FpC), 4.54 (Cp, CS$_2$FeCp); {^{1}H}^{13}C NMR (CDCl$_3$) δ 306.3 (FeCS$_2$Fe), 218.6 (CO, CpFe(CO)), 212.2 (CO, Fp), 82.2 (Cp), 79.7 (Cp).

Anal. Calcd for C$_{14}$H$_{10}$Fe$_2$O$_3$S$_2$: C,41.82; H,2.53. Found: C,41.66; H,2.32.

Reaction of $Cp(CO)_2Fe\text{-}CO_2^-Na^+$ (2) and $Cp(CO)_2FeI$.

Carbon dioxide (11.2 cc, 0.50 mmol) was introduced slowly by syringe into a THF solution of Fp^-Na^+ (0.30 mmol, 4.5 mL) that was maintained at -78 °C. The resulting yellow-brown solution of $FpCO_2^-Na^+$ (2) [11e] [IR after 2 min: $v(CO)$ 2000,1945 cm^{-1}] was treated with FpI (90 mg, 0.30 mmol). A red-brown solution was evident immediately; IR spectral monitoring within one minute of the cold solution indicated quantitative conversion to Fp_2: $v(CO)$ 1993, 1953, 1782 cm^{-1}. The solution was warmed to room temperature; the solvent was evaporated under reduced pressure; and the residue was extracted with 3x5 mL portions of diethyl ether. These combined ether extracts were passed through a 2 cm pad of alumina, which was further eluted with ether. The resulting purple filtrate was evaporated to leave 47 mg of purple brown crystals, for which the ^1H NMR spectrum indicated pure Fp_2 (89% yield).

Reaction of $Cp(CO)_2Fe\text{-}CO_2^-Li^+$ (2) and $Cp(CO)_2FeOSO_2CF_3$.

Fp(triflate) was prepared by adding $HOSO_2CF_3$ (0.29 mL, 3.25 mmol) over a 1 min period to a dichloromethane solution (30 mL) of $FpCH_3$ (0.625 g, 3.25 mmol). Reaction was instantaneous, as indicated by vigorous gas evolution; IR spectral monitoring was consistent with $FpCH_3$ quantitatively converting to $FpOSO_2CF_3$: $v(CO)$ 2078, 2032 cm^{-1}. The product was crystallized from a mixture of dichloromethane (7 mL) and 1:1 ether-hexane (30 mL) with scratching: 629 mg of dark purple crystals that were spectroscopically identified as $FpOSO_2CF_3$ [22], ^1H NMR ($CDCl_3$) δ 5.04 (Cp).

Fp(triflate) (400 mg, 1.20 mmol) was added to a THF solution of $FpCO_2^-Li^+$ (2), which was generated by adding CO_2 (33 cc, 1.50 mmol) to FpLi (15.0 mL, 1.00 mmol) at -78 °C [10c]. IR spectral analysis of the resulting cold, red-brown solution established complete conversion to Fp_2, which was isolated after column chromatography on activity 3 alumina (168 mg, 94% yield).

Reaction of $Cp(CO)_2Fe\text{-}CO_2^-Fe\text{-}CO_2^-Li^+$ (2) and $Cp(CO)_2FeHgCl$.

A THF solution of Fp^-Li^+ (1.00 mmol, 15 mL) was converted to $FpCO_2^-Li^+$ (2) using CO_2

(33 cc, 1.5 mmol) at -78 °C and then was treated with FpHgCl (0.412 g, 1.00 mmol). IR spectral monitoring of the resulting orange-brown solution that immediately formed was consistent with quantitative conversion of 2 to Fp_2Hg: IR 1985, 1959, 1925 cm^{-1}. Less than 5% of Fp_2 was detected by the presence of its bridging carbonyl $v(CO)$ at 1785 cm^{-1}. The solution was warmed to room temperature before evaporating the solvent and exhaustively extracting the residue with ether (4x6 mL). Combined extracts were concentrated to give orange-brown crystals (0.489 g) that were identified as spectroscopically pure Fp_2Hg [23] (90%): ^{1}H NMR (CDCl$_3$) δ 4.70 (Cp), vs δ 4.95 (Cp) for FpHgCl and δ 4.78 (Cp) for Fp_2.

Reaction of $Cp(CO)_2Fe\text{-}CO_2^-Na^+$ (2) with $Cp[P(OPh)_3](CO)FeI$.

A solution of Fp^-Na^+ in THF (1.00 mmol, 15.0 mL) was converted to $FpCO_2^-Na^+$ (2) at -78 °C and then was treated with $Cp(P(OPh)_3)(CO)FeI$ (586 mg, 1.00 mmol). IR spectral monitoring of the cold, red-brown solution was consistent with immediate conversion of 2 to Fp_2, as judged by the intensity of its bridging carbonyl $v(CO)$ at 1784 cm^{-1}. A weak absorption, $v(CO)$ 1757 cm^{-1}, was tentatively assigned to the mixed dimer $Cp_2Fe_2(CO)_3[P(OPh)_3]$,[24a] which however would be present only in low concentration (<15%). No further transformations occurred as established by IR spectral monitoring at room temperature. ^{31}P NMR spectra of the reaction mixture had major absorptions at δ 182.4 {$Cp_2Fe_2(CO)_3[P(OPh)_3]$} and at δ 168.4 {$Cp[P(OPh)_3](CO)FeI$}.

The crude reaction product was chromatographed on activity 3 alumina (neutral), eluting with 10-20% dichloromethane in hexane. Much decomposition was noted at the top of the column. A reddish purple band was eluted using 10% CH_2Cl_2; and a green band was removed using 15-20% CH_2Cl_2, with no other bands detected. The first band afforded spectroscopically pure Fp_2 (101 mg, 58% yield); the second band left 141 mg of $Cp[P(OPh)_3](CO)FeI$ as a green solid (24% recovery): IR (THF) 1981 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.28 (m, OPh), 4.21 (s, Cp); ^{31}P NMR (CDCl$_3$) δ 171.8.

As a control reaction, a THF solution of Fp^-Na^+ (3.0 mL, 0.18 mmol) was cooled to -78 °C and treated with $Cp[P(OPh)_3](CO)FeI$ (110 mg, 0.19 mmol). IR spectral monitoring of the cold,

red-brown solution was consistent with the presence of both Fp_2 and $Cp_2Fe_2(CO)_3[P(OPh)_3]$ [24] [$v(CO)$ 1992, 1954, 1784, 1757 cm^{-1}], although the proportion of Fp_2 to the mixed dimer increased with time: 3:2 (1 min), 1:1 (10 min), 1:1.2 (20 min at 0 °C to 1 h at 22 °C). Column chromatography of the residue on silica gel (2:1-1:1 hexane-benzene) or on activity 3 alumina (neutral) (5% ethyl acetate-hexane or 10% dichloromethane-hexane) did not adequately resolve the two red-brown bands. These were collected as one fraction, which afforded a dark red solid (58 mg) as a 1:1.2 mixture of Fp_2 and $Cp_2Fe_2(CO)_3[P(OPh)_3]$: ^1H NMR (CDCl$_3$) δ 4.80 and 4.08 (s, Cp, mixed dimer), 4.78 (s, Cp, Fp_2).

Reaction of $Cp(CO)_2Fe\text{-}CO_2^-Na^+$ (2) and $Cp(CO)Fe(CH_3CN)_2^+PF_6^-$.

A solution of Fp^-Na^+ in THF (1.0 mmol, 15.0 mL) was converted to a yellow-brown solution of $FpCO_2^-Na^+$ (2) at -78 °C, to which $Cp(CO)Fe(CH_3CN)_2^+PF_6^-$ (376 mg, 1.00 mmol) was added. The clear purple solution that resulted was examined by IR spectroscopy. Three products were immediately detected as a 2:1:1 mixture of Fp_2 [$v(CO)$ 1993, 1952, 1785 cm^{-1}], FpH [10a,25] [$v(CO)$ 2017, 1952 cm^{-1}], and an unidentified material [$v(CO)$ 1993, 1952, 1756 cm^{-1}]. IR spectra of this purple solution after sitting at 22 °C (20 min) indicated only the presence of Fp_2: its concentration had increased at the expense of the other two components. Ether extracts of the crude reaction mixture were chromatographed on alumina, from which a single red-brown band was eluted with ether. This afforded 285 mg of reddish purple crystals of spectroscopically pure Fp_2 (0.81 mmol). Considerable amounts of brown decomposition residues also were evident at the top of the column.

### Results and Discussion

Reactions of $FpCS_2^-$ (1)

We repeated Ellis', synthesis of Fp-C(S)S-Fp (3) (eq 1) as a control for subsequent reactions of $FpCS_2^-$ (1) and of $FpCO_2^-$ (2) with organoiron electrophiles. As reported [6], the reaction of 1 and FpI affords the stable $\mu(\eta^1\text{-}C{:}\eta^1\text{-}S)$ CS_2 adduct 3 in essentially quantitative yield. Table 1 contains ^{13}C NMR spectral data for 1 and 3, as well as for related CS_2- and CO_2-containing complexes.

The difference in chemical shifts for molecular CS_2 and CO_2 resembles the downfield trend that sp^2 carbons of organic thiones exhibit as compared to their carbonyl analogues. This downfield shift represents greater paramagnetic shielding for the carbon center of the CS double bond [26], a shift that also occurs for the metalloester $FpC(O)OCH_3$ and metallodithioester $FpC(S)SCH_2Ph$ compounds tabulated. Data for this dithioester complex also is similar to that of FpC(S)Fp (**3**).

Upon coordinating Fp⁻, CO_2 and CS_2 exhibit 85 and 107 ppm downfield shifts, respectively (Table 1). The resulting (η^1-C) metallodithiocarboxylate **1** and metallo-carboxylate **2** structures are consistent with IR spectral data (which preclude other reasonable structures [7]) and with theoretical arguments (for **1** [2a]). The chemical shifts for the heterocumulene centers on **1** and **2** indicate the extent of carbon hybridization and of charge delocalization involving the heteroatoms. Corresponding dimethoxycarbene and dithiomethoxycarbene compounds $[Fp\text{-}C(XCH_3)_2]^+$ (X=O, S), which have considerable charge delocalization, also display downfield shifts of their carbon centers.

The ^{13}C NMR spectral data for **1** also compares with that of the anionic tungsten CO_2 adduct $(CO)_5WCO_2{}^{2-}$, δ 223.4 in THF. Cooper [4a] demonstrated that NMR and IR spectral data support a superposition of the resonance structures for this adduct,
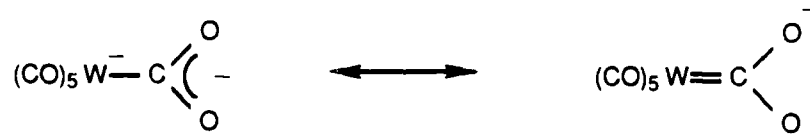

The IR spectrum resembles those of anionic pseudohalide complexes, e.g., $(CO)_5WOC(O)CH_3{}^-$, in which the charge localizes on the $W(CO)_5$ moiety. The magnitude of the coupling constant $J_{W\text{-}C}$ for the CO_2 center on $(CO)_5WCO_2{}^{2-}$ indicates extensive W=C double bonding, thus favoring charge localization on the oxygens.

The bis-iron μ-(η^1-C:η^2-S,S') CS_2 complex, Fp-C(S)S-Fe(CO)Cp (**4**), because of the presence of its chelating dithiocarboxylate structure, served as a synthetic objective. Busetto and

coworkers [9] demonstrated the thermodynamic stability that is associated with such chelating ligands; for example, Fp-C(S)S-Mn(CO)$_5$ spontaneously transforms into its chelated derivative Fp-C(S)S-Mn(CO)$_4$ [9b]. We prepared 4, a known compound [9c], from the reaction between FpCS$_2^-$ (1) and an appropriate organoiron electrophile. This methodology then would be extended to synthesizing the congeneric μ-CO$_2$ compound 5. (Most of the known bimetallic and trimetallic CO$_2$ complexes retain similar analogous chelated metallocarboxylate structures [13].)

We selected Cp(CO)Fe(CH$_3$CN)$_2^+$PF$_6^-$ [19] as the organometallic Lewis acid of choice [14] — one that bears two accessible coordination sites — to convert the CS$_2$ complex 1 to 4 (eq 3). In previous studies, we documented that this labile bis-acetonitrile complex readily exchanges
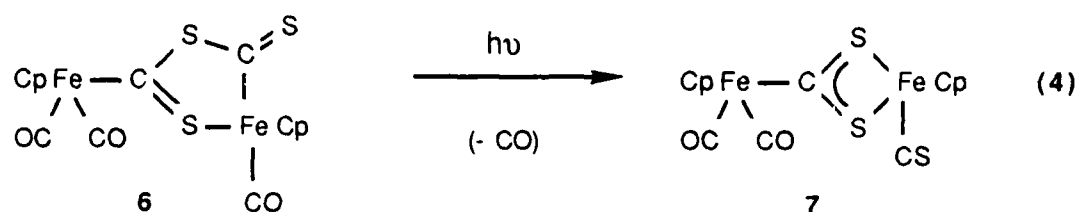
(3)

1   4
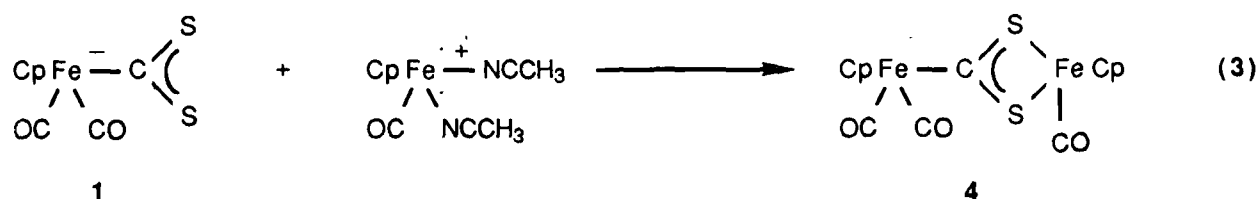
its ligated acetonitrile for a variety of phosphines and phosphites in dichloromethane [19b], an exchange that can be carried out stepwise in order to bind two different phosphorus-donor ligands. A particularly relevant observation [19b] is that the room-temperature reaction between Cp(CO)Fe(CH$_3$CN)$_2^+$ PF$_6^-$ and Et$_2$NCS$_2^-$Na$^+$ in THF selectively affords the (η^2-S,S') chelate Cp(CO)Fe-SC(S)NEt$_2$ (73% yield) that is uncontaminated by the Fp (η^1-S) dithiocarbamate Cp(CO)$_2$Fe-SC(S)NEt$_2$.

L$_1$, L$_2$ = PR$_3$
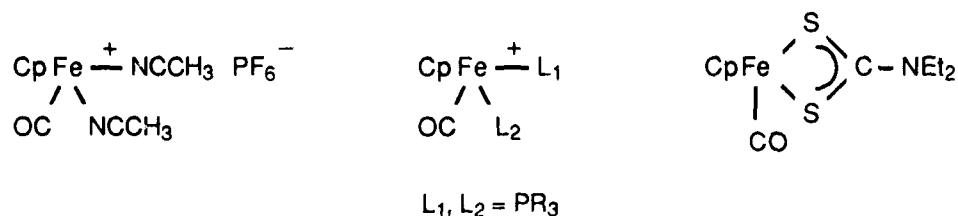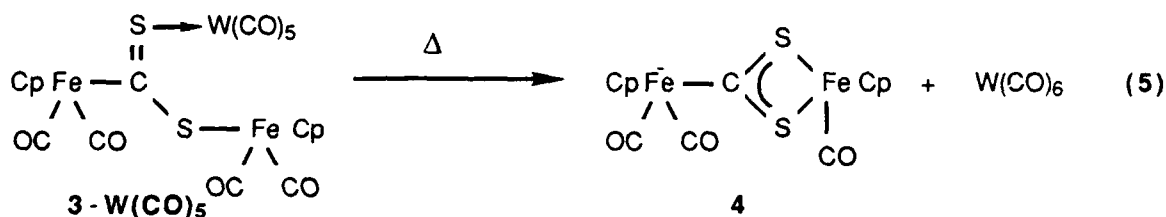
Treatment of the same labile bis-acetonitrile salt with FpCS$_2^-$K$^+$ (1) in THF (-78 °C) gives the desired μ(η^1-C:η^2-S,S') dithiocarboxylate 4 in moderate yield. The actual yield corresponding to 4 isolated by column chromatography, however, varied between 21 and 45% in

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six experiments.

Near insolubility of the bis-acetonitrile iron reagent, particularly at lower temperatures, could account for the moderate yields observed. A sluggish reaction (eq 3), whatever the cause, expedites deleterious side reactions that are attributed to decomposition of 1 (above -20 °C) and of $Cp(CO)Fe(CH_3CN)_2^+$ PF_6^- in THF. We previously noted that this bis-acetonitrile salt degrades in THF (as a suspension at room temperature) to an intermediate that has been formulated as $Cp(CO)(THF)Fe(CH_3CN)^+$, which then rapidly decomposes to insoluble residues.[19b]

Reaction between $FpCS_2^-Na^+$ (1-Na$^+$) and $Cp(CO)Fe(CH_3CN)_2^+$ PF_6^- under otherwise identical conditions affords complex mixtures. These were not adequately separated by column chromatography; ^1H NMR spectral analysis of the crude reaction mixture indicated the presence of 6-10 CpFe singlets (δ 5.2 - 4.50) of comparable intensities.

IR and ^1H NMR spectral data for the stable red solid resulting from the reaction of $FpCS_2^-$ K$^+$ (1) and $Cp(CO)Fe(CH_3CN)_2^+$ matches that previously reported for 4 [9c]. The presence of three carbonyl stretching frequencies [2025, 1989 cm^{-1} for Fp, and 1938 cm^{-1} for Cp(CO)Fe] and of the expected [9] two thiocarboxylate $v(CS_2)$ absorptions [914, 875 cm^{-1}] for chelating dithiocarboxylate are particularly diagnostic. These absorptions closely correspond to similar values reported for the thiocarbonyl analogue 7 (eq 4): $v(CO)$ 2030, 1987 cm^{-1}; $v(CS_2)$ 913, 880 cm^{-1}. Our ^{13}C NMR spectral data for 4 resembles that of 6 [27*] and of [FpC(SFp)-(SCH$_3$)]$^+$ [8d], with their corresponding Fp-bound dithiocarboxylate carbons producing signals at δ 306, 329, and 315, respectively.

6   7   (4)

Busetto and coworkers [9c] previously obtained 4 from the thermal decomposition of the W(CO)$_5$-adduct of 3 (eq 5). Under the relatively mild conditions of this reaction (refluxing dichloromethane, 40 °C), W(CO)$_5$-3 affords 4 in 70% yield. In contrast, thermolysis of FpC(S)SFp (3) requires refluxing octane (126 °C) before extruding CS_2 and leaving Fp_2.

$$3 \text{-} W(CO)_5 \xrightarrow{\Delta} 4 + W(CO)_6 \qquad (5)$$

Photolysis of **3** also is reported to give **4** in 17% yield [9c]. We repeated this photolysis in benzene and in THF (+5 °C) using both a Rayonet photochemical reactor (λ 3550 Å) and a Hanovia medium-pressure mercury-vapor lamp. In all cases starting material was consumed, but isolated yields of **4** after column chromatography uniformly were less than 10%. Dimeric Fp_2 appears as the other major isolated product (less than 10% yield); other decomposition products(s) do not elute from silica gel chromatography columns.

Reactions of $FpCO_2^-$ (2)

Bis-iron $\mu(\eta^1\text{-}C{:}\eta^1\text{-}O)$ CO_2 complexes **5a-c** offer plausible synthetic objectives in view of the thermal stability of the CS_2 congener **3**. Complex **5a** should retain $(\eta^1\text{-}C)$ and $(\eta^1\text{-}O)$ bonding analogous to that found in the stable methyl ester, $Fp\text{-}C(O)OCH_3$ [10b], and acetate, $Fp\text{-}OC(O)CH_3$ [28], complexes. These structural features will prevail only if structures **5a-c** do not

5 (a) L = CO
(b) L = P(OPh₃)
(c) L = PPh₃
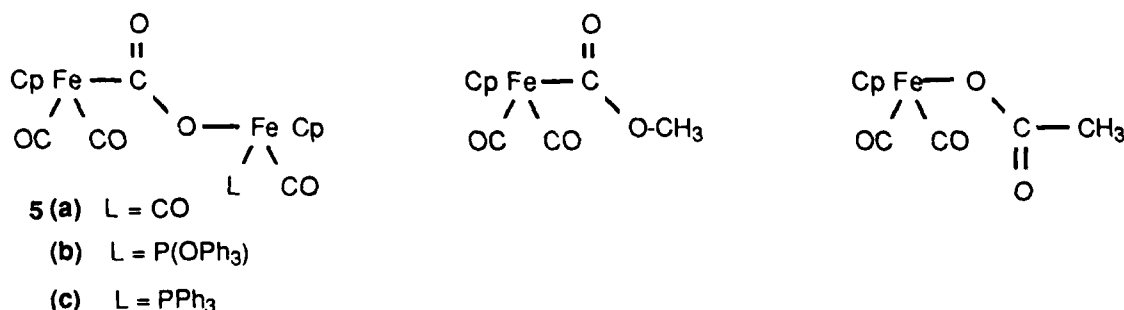
readily extrude CO_2 and leave the iron-iron dimer Fp_2. A similar thermodynamic driving force occurs with related bimetallic ethane-1,2-diyl complexes $M\text{-}CH_2CH_2\text{-}M$, which commonly release M_2 and ethylene [29].

Fp(methylester) and Fp(acetate) complexes also serve as useful models in terms of relating their IR spectral data to that anticipated for **5a**. Since their moderately intense ester and acetate IR $v(CO)$ absorptions appear at 1647 and 1617 cm^{-1}, respectively, we expect that **5a** would have a similar absorption in the region of 1600-1650 cm^{-1} [30*]. This IR spectral region is particularly convenient to monitor as it is devoid of terminal carbonyl absorptions (2040-1940 cm^{-1}), which typically overlap in mixtures of Fp-X compounds. The bridging carbonyl $v(CO)$ for Fp_2 appears at 1784 cm^{-1} (THF), and similar absorptions for binuclear complexes $Cp_2(CO)_3Fe_2(L)$ [L=P(OPh), and PPh_3] [24] also anticipated byproducts in attempted syntheses of **5b,c**, appear within 1700-1750 cm^{-1}.

Our synthetic approach involved reacting THF solutions of $FpCO_2^-$ (**2-Na$^+$** and **2-Li$^+$**) at -78 °C with the organoiron electrophiles (eq 6) and then immediately monitoring the cold solutions by IR spectroscopy, with particular attention accorded to the 1600-1650 cm^{-1} region. Initial IR data typically were recorded within 2 minutes of mixing **2** and the iron Lewis acid and at an IR cell temperature of ca. 0 °C.

$$\text{CpFe} - \text{C} \underset{\underset{OC \quad CO}{\diagup \diagdown}}{\overset{O}{\diagup}} \overset{O}{\diagdown} \quad + \quad \text{Cp Fe} - \text{X} \underset{\underset{L \quad CO}{\diagup \diagdown}}{} \longrightarrow \text{Cp Fe} - \text{Fe Cp} \quad + \cdots \quad (6)$$

2 Li$^+$	L = CO, X= I, OSO_2CF_3
2 Na$^+$	L = P(OPh)$_3$, X = I
	L= PPh3, X = I
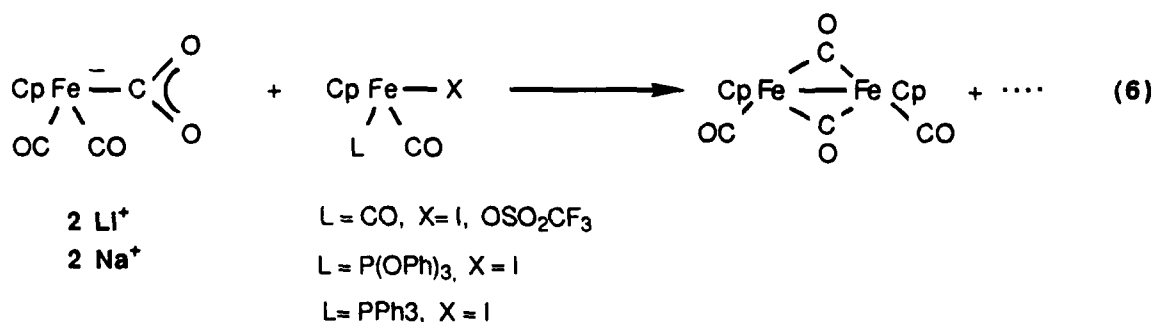
Treatment of $FpCO_2^-$ (**2-Li$^+$**, **2-Na$^+$**) with either FpI or Fp(triflate) at -78 °C immediately and quantitatively affords Fp_2. Isolated yields of Fp_2 after column chromatography were routinely 85-95%, increasing slightly with the scale of the reaction. Attempts to use $Fp(THF)^+BF_4^-$ [33] as the organoiron electrophile were thwarted by its insolubility in THF at -78 °C. After reacting it with **2-Li$^+$** (0.50 mmol scale) for 10 minutes and filtering the cold suspension, we recovered 94% of the starting $Fp(THF)^+$ salt. An IR spectrum of the supernatent solution indicated quantitative conversion of **1-Li$^+$** to Fp_2.

The reaction between **2-Li+** or **2-Na+** and Cp[P(OPh)$_3$](CO)FeI likewise produces Fp$_2$ as the predominant organometallic species, although small amounts (10%) of the phosphite-substituted dimer Cp$_2$Fe$_2$(CO)$_3$[P(OPh)$_3$] (**8**) [24a] also forms. Concentrations of this mixed dimer, estimated by IR spectral monitoring, did not change during the course of the reaction, 2 min (-78 °C) to 1 h (+22 °C). ^{31}P NMR spectra of the crude reaction mixture at room temperature established the presence of this dimer as well as the starting iron-iodide complex. A typical chromatographic workup of the reaction between **2-Na+** and Cp[P(OPh)$_3$](CO)FeI delivers Fp$_2$ (58% yield) and starting iron iodide (24% recovery) in addition to considerable amounts of decomposition residues.

Reaction between Fp⁻Na+ and Cp[P(OPh)$_3$](CO)FeI under otherwise identical conditions gives different results (eq 7). Substantial amounts of phosphite-substituted dimer **8** along with Fp$_2$ are evident even in the early stages of the reaction. The concentration of Cp$_2$Fe$_2$(CO)$_3$[P(OPh)$_3$] (**8**) increases with time at the expense of Fp$_2$, so that at room temperature (1 h elapsed time) a final 1:1.2 mixture of Fp$_2$ to **8** prevails.
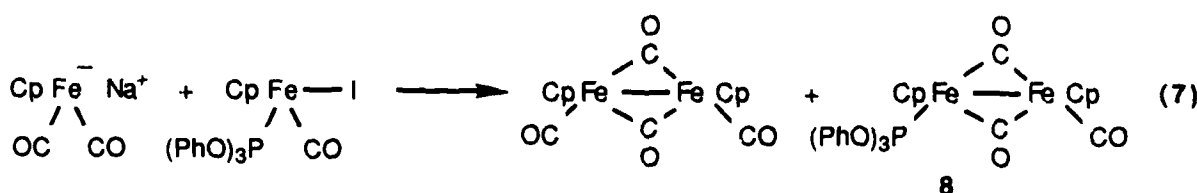
Results for the Fp⁻Na+ / Cp[P(OPh)$_3$](CO)FeI reactions are complicated. A straight-forward coupling of the two iron centers does not occur since approximately 50% of the reaction product is Fp$_2$. Of the Cp$_2$Fe$_2$(CO)$_3$[P(OPh)$_3$] (**8**) that does form, at least 16% (and quite possibly more) of it derives from the Fp$_2$. This mixed dimer **8** apparently doesn't result from Fp⁻ promoting CO displacement on Fp$_2$, since treating Fp$_2$ / P(OPh)$_3$ mixtures (1:2) with 0.10 or 1.0 molar equivalents of Fp⁻Na+ in THF (-20 °C) does not give any detectable **8**. Others previously noted that Fp$_2$ is thermally unreactive towards phosphines and phosphites at room temperature [24].
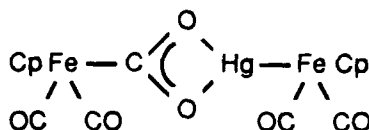
Metallocarboxylate FpCO$_2$⁻Na+ (**2**) and metalate Fp⁻Na+ afford different product mixtures upon combining with Cp[P(OPh)$_3$](CO)FeI. The reaction involving **2** (eq 6) produces very little of Cp$_2$Fe$_2$(CO)$_3$[P(OPh)$_3$] (**8**) even though it is stable under the experimental conditions. Isolation

of Fp_2 as the major product is consistent with **2** interacting with the iron iodide by an electron transfer process that ultimately affords 17-electron intermediates $Cp(L)(CO)Fe\cdot$ (L=CO, $P(OPh)_3$). Others have established that these substituted odd-electron species (e.g., $L=P(OPh)_3$), which remain after ligand dissociation from 19-electron intermediates $Cp(L)(CO)FeX^{\bar{\cdot}}$ or $Cp(L)(CO)_2Fe\cdot$ [34], preferentially give unsubstituted dimer Fp_2 [12a*,35]. The main observation is that $FpCO_2^-$ (**1**) does not dissociate CO_2 and react as Fp^- with $Cp[P(OPh)_3](CO)FeI$, although further mechanistic studies clearly are needed.

This electron transfer process also could account for the Fp_2 product that results from treating $FpCO_2^-Na^+$ (**2**) with FpI or Fp(triflate). Electron transfer affords odd-electron transient species FpX^- and $(FpCO_2)\cdot$ that degrade to the 17-electron $Fp\cdot$, which dimerizes. Lee and Cooper [11b] advanced a similar mechanism to account for their observation that $FpCO_2^-Li^+$ (**2**) reacts with $FpCO^+BF_4^-$ to give exclusively Fp_2.

Reactions between the triphenylphosphine-substituted iron iodide, $Cp(PPh_3)(CO)FeI$, and $FpCO_2^-Na^+$ (**2**) or Fp^-Na^+ afford results that are very similar to those observed for the phosphite- containing analogue $Cp[P(OPh)_3](CO)FeI$, as ascertained by IR spectral monitoring. The documented thermal instability of the mixed dimer $Cp_2Fe_2(CO)_3(PPh_3)$ at room temperature [24b] precluded further analysis or workup of these reactions, however.

We examined the reaction of FpHgCl with $FpCO_2^-Li^+$ (**2**) in an attempt to generate an $(\eta^2\text{-}O,O')$ Fp(carboxylate)-Hg(II) derivative. Electrophilic FpHgCl had been used in forming metal-Hg(II) bonds to metal clusters[36] (the $FpHg^+$ intermediate is isolobal with H^+,CH_3^+, or

$$CpFe-C\underset{\underset{OC\quad CO}{\diagup\diagdown}}{\overset{\overset{O}{\diagup\diagdown}}{}}\underset{O}{\diagdown}Hg-Fe\,Cp\underset{OC\quad CO}{\diagup\diagdown}$$

$(PPh_3)Au^+$). Our reaction, however, promptly and quantitatively generated Fp_2Hg.

Treatment of the labile bis-acetonitrile salt $Cp(CO)Fe(CH_3CN)_2^+PF_6^-$ with $FpCO_2^-Na^+$ (**2**) (eq 8) initially generates a complex mixture of Fp_2, FpH [10b,25], and an unidentified component having a bridging carbonyl $\nu(CO)$ at 1756 cm^{-1} (eq. 8). Upon warming this mixture to room temperature, only Fp_2 is evident during IR spectral monitoring (isolated yield 41%).

$$\text{(8)}$$
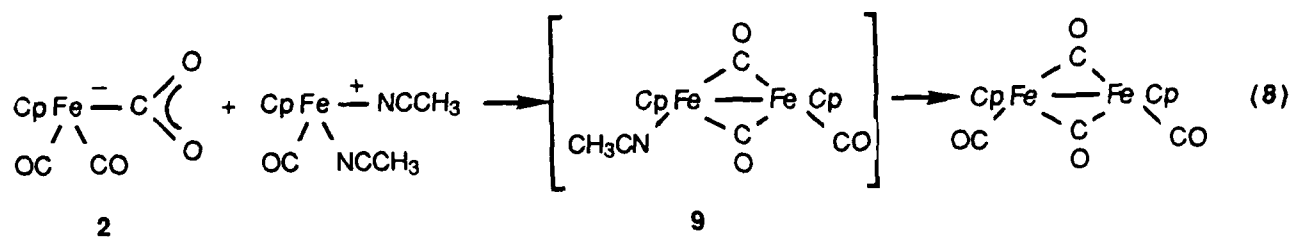
We formulate the unidentified component as the mono-acetonitrile adduct of Fp_2: $Cp_2Fe_2(CO)_3(CH_3CN)$ (9). Related dimers $Cp_2Fe_2(CO)_3[P(OPh)_3]$ (8) and $Cp_2Fe_2(CO)_3PPh_3$ likewise exhibit lower energy bridging carbonyl $\nu(CO)$ at 1757 and 1733 cm^{-1} (with respect to Fp_2, $\nu(CO)$ 1782 cm^{-1}, also in THF). Labinger [37] previously prepared 9 by photolysis of Fp_2 in acetonitrile and documented its solution instability.
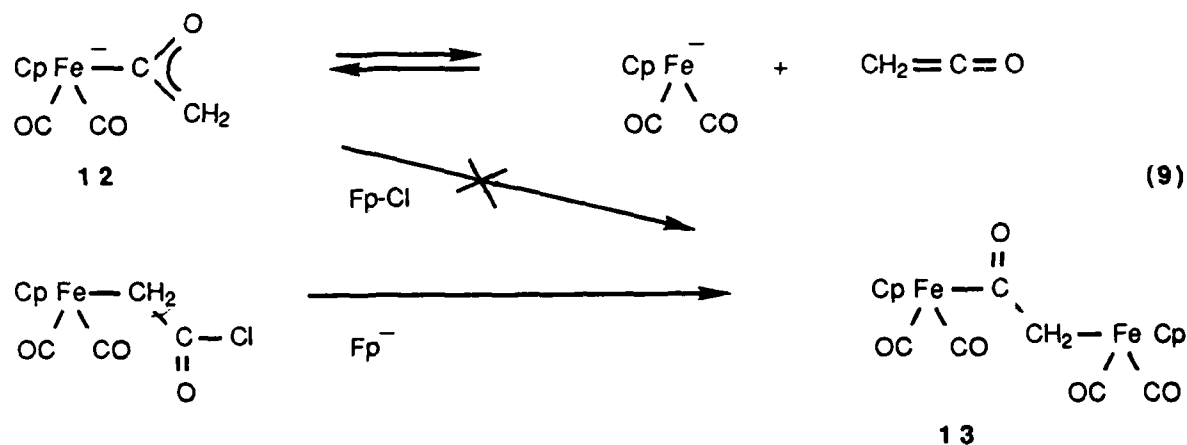
Our inability to generate the chelating bis-iron $\mu(\eta^1\text{-}C:\eta^2\text{-}O,O')$ CO_2 complex 6 raised the question: could analogous chelating organic carboxylate complexes 10 be prepared? Werner [38] reported that corresponding molybdenum and tungsten acetate chelates 11 are the stable products of warming the $(\eta^1\text{-}O)$ acetates $Cp(CO)_3M\text{-}OC(O)CH3$.
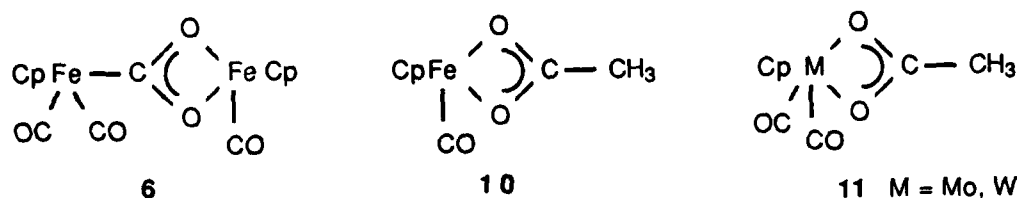
We found that the bis-acetonitrile salt $Cp(CO)Fe(CH_3CN)_2^+$ PF_6^- is inert to the carboxylate salts $PhCO_2^-Li^+$, $Me_3CCO_2^-Li^+$, $PhCH_2CO_2^-Li^+$ and $PhCO_2^-Na^+$ in THF solution. These carboxylates remain unchanged (IR spectral monitoring of $\nu(CO_2)$ region 1550 to 1620 cm^{-1}) as the iron-acetonitrile complex degrades (1 h, 20 °C) to insoluble residues. Attempts to prepare the chelating acetate complex 10 ($R=CH_3$) by photolysis of $FpOC(O)CH_3$ also failed. Irradiation (Rayonet Reactor, 3500 Å) in either benzene or THF solution (10 °C) degraded Fp acetate to Fp_2 and insoluble residues.

Reaction chemistry of $FpCO_2^-$ (2) resembles that of the $(\eta^1\text{-}C)$ ketene complex $Fp(CH_2CO)^-$ (12). Helquist [39] first generated this heterocumulene adduct by deprotonating

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FpCOCH$_3$ at low temperature, and Akitah and coworkers [31] demonstrated that **12** equilibrates with Fp$^-$ and free ketene above -50 °C. Attempts to intercept **12** with FpCl and generate FpC(O)CH$_2$-Fp (**13**) produced only Fp$_2$ (eq 9). The desired μ-ketene compound **13** does form,

(9)

however, by metallating the chloroacetyl compound FpCH$_2$C(O)Cl with Fp$^-$; the resulting **13** is a thermally stable molecule that only extrudes ketene after photolysis. Our inability to generate μ-CO$_2$ compounds **5** and **6** likewise may not be due to their thermodynamic instability, but may indicate a need to alter the synthetic approach.

Conclusions

We did not convert the metallocarboxylate FpCO$_2^-$ (**2**) to bimetallic CO$_2$ adducts FpC(O)OFp (**5a**) or Fp-C(O)O-Fe(CO)Cp (**6**) under conditions that the corresponding μ-CS$_2$ adducts **3** and **4**, respectively, readily form using FpCS$_2^-$ (**2**). Either **5** or **6** could have been transient intermediates that quickly degraded, perhaps by a pathway involving odd-electron organometallic intermediates. We disfavor this explanation because there is no apparent reason why **5** and **6**, once formed, should be less stable than their CS$_2$ congeners or even the μ-ketene compound FpC(O)CH$_2$-Fp (**13**) [40]. A more plausible interpretation of our results is that FpCO$_2^-$ (**2**) reacts with the organoiron electrophiles by an alternative pathway not involving either prior dissociation of CO$_2$ or coupling or **2** and the metal Lewis acid.

References

1. (a) D. Walther, Coord. Chem. Rev., 79 (1987) 135. (b) D. J. Darensbourg and R. A. Kudaroski, Adv. Organomet. Chem., 22 (1983) 129. (c) A. Behr In W. Keim (Ed.), Catalysis in C1 Chemistry; D. Reidel Publishers, Boston, 1983; p 169. (d) T. Ito and A. Yamamoto In S. Inoue and N. Yamazaki (Eds.), Organic and Bio-Organic Chemistry of Carbon Dioxide; Wiley, New York, 1982; Chapter 3. (e) R. P. A. Sneedon In G. Wilkinson, F. G. A. Stone and F. W. Abel (Eds.), Comprehensive Organometallic Chemistry; Vol. 8; Pergamon, New York, 1982; Chapter 50.4.

2. (a) C. Bianchini, C. Mealli, A. Meli and M. Sabat In I. Bernal (Ed.), Stereochemistry of Organometallic and Inorganic Compounds; Elsevier, New York, 1986; Chapter 3. (b) J. A. Ibers, Chem. Soc. Rev. 11 (1982) 57. (c) H. Werner, Coord. Chem. Rev., 43 (1982) 165.

3. Theoretical studies stressing coordination of CO2 and CS2 to transition organometallic fragments: (a) S. Sakaki, K. Kitaura and K. Morokuma, Inorg. Chem., 21 (1982) 760. (b) C. Mealli, R. Hoffmann and A. Stockis, Inorg. Chem., 23 (1984) 56. (c) T. Ziegler, Inorg. Chem., 25 (1986) 2721. (d) M. Rosi, A. Sgamellotti, F. Tarantelli and C. Floriani, Inorg. Chem., 26 (1987) 3805; J. Organomet. Chem., 332 (1987) 153.

4. Complementary pairs of CO_2-CS_2 transition organometallic complexes that have been studied include, (a) $(CO)_5W(CX_2)^{2-}$: G. R. Lee, J. M. Maher and N. J. Cooper, J. Am. Chem. Soc., 109 (1987) 2956. (b) $Cp_2(PMe_3)Ti(CX_2)$: H. G. Alt, K.-H. Schwind and M. D. Rausch, J. Organomet. Chem., 321 (1987) C9. (c) $N(CH_2CH_2 PPh_2)_3Co(CX_2)^{+q}$ (q=0,X=S; q=1, X=O): C. Bianchini and A. Meli, J. Am. Chem. Soc., 106 (1984) 2698. C. Bianchini, A. Meli and G. Scapacci, Organometallics, 2 (1983) 1834.

5. J. E. Ellis, R. W. Fennel and E. A. Flom, Inorg. Chem., 15 (1976) 2031.

6. G. O. Evans, W. F. Walter, D. R. Mills and C. A. Streit, J. Organomet. Chem., 144 (1987) C34.

7. A. R. Cutler, P. K. Hanna and J. C. Vites, Chem. Rev., in press.

8. (a) L. Busetto, U. Belluco and R. J. Angelici, J. Organomet. Chem., 18 (1969) 213. B. D. Dombek, R. J. Angelici, I. S. Butler and D. Cozak, Inorg. Synth., 17 (1977) 100. (b) T. A. Wnuk and R. J. Angelici, Inorg. Chem., 16 (1977) 1173. (c) F. B. McCormick and R. J. Angelici, Inorg. Chem., 18 (1979) 1231. (d) H. Stolzenberg, W. P. Fehlhammer, M. Monari, V. Zanotti and L. Busetto, J. Organomet. Chem., 272 (1984) 73. (e) R. J. Angelici and J. W. Dunker, Inorg. Chem., 24 (1985) 2209.

9. (a) H. Stolzenberg and W. P. Fehlhammer, J. Organomet. Chem., 235 (1982) C7. (b) L. Busetto, A. Palazzi and M. Monari, J. Chem. Soc., Dalton Trans., (1982) 1631. (c) L. Busetto, M. Monari, A. Palazzi, V. Albano and F. Demartin, J. Chem. Soc., Dalton Trans.,(1983) 1849.

10. (a) T. Bodnar, E. Coman, K. Menard and A. Cutler, Inorg. Chem., 21 (1982) 1275. (b) T. Forschner, K. Menard and A. Cutler,. J. Chem. Soc., Chem. Commun., (1984) 121. (c) M. E. Giuseppetti and A. R. Cutler, Organometallics, 6 (1987) 970.

11. (a) G. R. Lee and N. J. Cooper, Organometallics, 4 (1985) 794. (b) G. R. Lee and N. J. Cooper, Organometallics, 4 (1985) 1467.

12. Gibson recented reported that the more electron-rich metallocarboxylate $Cp(PPh_3)(CO)Fe\text{-}CO_2^-K^+$, which is available from the pH-dependent hydrolysis of the carbonyl salt $Cp(PPh_3)Fe(CO)_2^+$, undergoes methylation (MeI or $MeOSO_2CF_3$) and gives the metalloester $Cp(PPh_3)Fe(CO)FeCO_2CH_3$. Gladysz similarly noted that $Cp(PPh_3)(NO)ReCO_2^-Li^+$ affords tin- or germanium-containing metalloesters $Cp(PPh_3)(NO)Re\text{-}C(O)OMPh_3$. The only other example of alkylating a metallo-carboxylate is Herskovitz's early communication on methylating $(PMe_2CH_2CH_2PMe_2)_2IrCO_2$ with $MeOSO_2F$. (a) D. H. Gibson and T.-S. Ong, Ibid., 109 (1987) 7191. (b) D. R. Senn, K. Emerson, R. D. Larsen and J. A. Gladysz, Inorg. Chem., 26 (1987) 2737. (c) R. L. Harlow, J. B. Kinney and T. Herskovitz, J. Chem. Soc., Chem. Commun.,(1980) 813.

13. (a) E. Fujita, D. J. Szalda, C. Creutz and N. Sutin, J. Am. Chem. Soc., 110 (1988) 4870. (b) C. C. Tso and A. R. Cutler, J. Am. Chem. Soc., 108 (1986) 6069. (c) A. Doehring, P. W. Jolly, C. Krueger and M. J. Romao, Z. Naturforsch., B: Anorg. Chem., Org. Chem., 40B (1985) 484. (d) J. D. Audett, T. J. Collins, B. D. Santarsiero and

19

G. H. Spies, J. Am. Chem. Soc., 104 (1982) 7352. (e) A number of trinuclear / cluster systems with ligated CO_2 also have been characterized: E. G. Lundquist, J. C. Huffman and K. G. Caulton, J. Am. Chem. Soc., 108 (1986) 8309. K. Raab and W. Beck, Chem. Ber., 118 (1985) 3830. G. R. John, B. F. G. Johnson, J. Lewis and K. C. Wong, J. Organomet. Chem., 169 (1979) C23.

14. W. Beck and K. Sunkel, Chem. Rev., 88 (1988) 000.

15. D. F. Shriver and M. A. Drezdzon, The Manipulation of Air-Sensitive Compounds; 2nd ed.; Wiley-Interscience, New York, 1986.

16. R. B. King, Organometallic Syntheses; Vol. 1; Academic Press, New York, 1965.

17. M. J. Mays and J. D. Robb, J. Chem. Soc. A, (1986) 329.

18. J. A. Gladysz, G. M. Williams, W. Tam, D. L. Johnson, D. W. Parker and J. C. Selover, Inorg. Chem., 18 (1979) 553.

19. (a) D. Catheline and D. Astruc, J. Organomet. Chem., 272 (1984) 417. (b) A. B. Todaro, A. R. Cutler and J. J. Benoit, manuscript submitted.

20. D. A. Brown, H. J. Lyons, A. R. Manning and J. M. Rowley, Inorg. Chim. Acta, 3 (1969) 346. D. A. Brown, H. J. Lyons and A. R. Manning, Inorg. Chim. Acta, 4 (1970) 428. R. J. Haines, A. L. DuPreez and L. L. Marais, J. Organomet. Chem., 28 (1971) 405.

21. P. M. Treichel, R. L. Shubkin, K. W. Barnett and D. Reichard, Inorg. Chem., 5 (1966) 1177.

22. M. B. Humphrey, W. M. Lamanna and M. Brookhart, Inorg. Chem., 22 (1983) 3355. K.-H. Griessmann, A. Stasunik, W. Angerer and W. Malisch, J. Organomet. Chem., 303 (1986) C29. M. Appel, K. Schloter, J. Heidrich and W. Beck, J. Organomet. Chem., 322 (1987) 77.

23. J. M. Burlitch and A. Ferrari, Inorg. Chem., 9 (1970) 563, and references cited therein.

24. (a) R. J. Haines and A. L. DuPreez, Inorg. Chem., 8 (1969) 1459. F. A. Cotton, L. Kruczynski and A. J. White, Inorg. Chem., 13 (1974) 1402. F. A. Cotton, B. A. Frenz and A. J. White, Ibid., 13 (1974) 1407. (b) A. J. White, J. Organomet. Chem., 168 (1979) 197.

25. S. B. Fergusson, L. J. Sanderson, T. A. Shackleton and M. C. Baird, Inorg. Chim. Acta, 83 (1984) L45.

26. E. Breitmaier and W. Voelter, 13C NMR Spectroscopy; 2nd ed.; Verlag Chemie, New York, 1978; p 181.

27. (a) Complex 6 bearing a five member FeC_2S_2 ring results from the condensation of Fp-C(S)S-Fp (3) and $FpCS^+$, followed by cleavage of the thione-coordinated Fp^+ with NaI in refluxing acetone. ^{13}C NMR spectral data is available for 6 (but not for 7). We inverted Busetto's assignments [27b] for the FeC_2S_3 ring, δ 279.2 and 329.5, in order to retain internal consistency with the data in Table 1. The thione carbons in Fp-C(S)SCH$_2$Ph and in 6 thus appear at δ 287.6 and 279.5, respectively. (b) L. Busetto, V. Zanotti, V. G. Albano, D. Braga and M. Monari, J. Chem Soc., Dalton Trans., (1987) 1133.

28. C.C. Tso and A. R. Cutler, Organometallics, 4 (1985) 1242.

29. (a) W. Beck and B. Olgemöller, J. Organometal. Chem., 127 (1977) C45. B. Olgemöller and W. Beck, Chem. Ber., 114 (1981) 867. (b) C. P. Casey and J. D. Audett, Chem. Rev., 86 (1986) 339.

30. For comparison, the binuclear $\mu(\eta^1$-C:η^1-C') ketene complex Fp-CH$_2$C(O)-Fp (13) [31] exhibits its C_2-ligand carbonyl ν(CO) at 1612 cm^{-1} (CH$_2$Cl$_2$), vs similar absorptions at 1647 cm^{-1} for Fp-COCH$_3$ and at 1658 cm^{-1} for Fp-CH$_2$C(O)CH$_3$ [32]. The two electron-rich iron centers on FpCH$_2$COFp evidently reinforce one another in diminishing the organic carbonyl bond order.

31. (a) M. Akita, A. Kondoh, K. Takashi, Y. Moro-Oka, J. Organometal. Chem., 299 (1986) 369. (b) M. Akita, A. Kondoh and Y. Moro-oka, J. Chem. Soc., Chem. Commun., (1986) 1296. M. Akita, A. Kondoh, T. Kawahara, T. Takagi and Y. Moro-oka, Organometallics, 7 (1988) 366

32. J. K. P. Ariyaratne and M. L. H. Green, J. Chem. Soc., (1964) 1.

33. (a) D. L. Reger and C. Coleman, J. Organomet. Chem., 131 (1977) 153. (b) E. K. G. Schmidt and C. H. Thiel, J. Organomet. Chem., 220 (1981) 87. (c) M. Rosenblum and D. Scheck, Organometallics, 1 (1982) 397. (d) N. Kuhn and H. Schumann, J. Organomet. Chem., 276 (1984) 55; 304 (1986) 181. H. Schumann, ibid., 299

(1986) 169. (e) H. Schumann, J. Organomet. Chem., 293 (1985) 75.

34. J. P. Blaha and M. S. Wrighton, J. Am. Chem. Soc., 107 (1985) 2694. A. S. Goldman and D. R. Tyler, Inorg. Chem., 26 (1987) 253. M. J. Therien and W. C. Trogler, J. Am. Chem. Soc., 109 (1987) 5127. J. Morrow, D. L. Catheline, M.-H. Desbois, J.-M. Manriquez, J. Ruiz and D. Astruc, Organometallics, 6 (1987) 2605.

35. P. L. Bogdan, A. Wong and J. D. Atwood, J. Organomet. Chem., 229 (1982) 185. B. D. Fabian and J. A. Labinger, Organometallics, 2 (1983) 659. J. A. Armstead, D. J. Cox and R. Davis, J. Organomet. Chem., 236 (1982) 213. N. J. Coville, E. A. Darling, A. W. Hearn and P. Johnston, J. Organomet. Chem., 328 (1987) 375.

36. J. Wang, M. Sabat, C. P. Horwitz and D. F. Shriver, Inorg. Chem., 27 (1988) 552.

37. J. A. Labinger and S. Madhaven, J. Organomet. Chem., 134 (1977) 381.

38. H. Werner, J. Roll, R. Zolk, P. Thometzek, K. Linse and M. Ziegler, Chem. Ber., 120 (1987) 1553.

39. K. Brinkman and P. Helquist, Tetrahedron Lett., (1985) 26.

40. A related (η^2-O,O') acetylacetonate chelate (η^5-C$_5$Me$_5$)(CO)FeOC(CH$_3$)CHC(CH$_3$)O has been characterized: E. E. Bunel, L. Valle and J. M. Manriquez, Organometallics, 4 (1985) 1680.

Table 1 ^{13}C NMR Spectral Assignments (δ)

	δ (CDCl$_3$)	Reference
O=C=O	132.0	a
S=C=S	192.5	a
CpFe–C(O)(O) ... Li$^+$ (**2**), (OC)(CO)	217.0	b,c
CpFe–C(S)(S) K$^+$ (**1**), (OC)(CO)	308.9	b,d
CpFe–C(=O)–O–CH$_3$, (OC)(CO)	213.3	c
CpFe–C(=S)–S–CH$_2$Ph, (OC)(CO)	287.6	e
CpFe–C(OCH$_3$)(OCH$_3$)$^+$ PF$_6^-$, (OC)(CO)	251.9	f
CpFe–C(SCH$_3$)(SCH$_3$)$^+$ PF$_6^-$, (OC)(CO)	304.3	f
CpFe–C(=S)–S–FeCp (**3**), (OC)(CO)(OC)(CO)	298.2	d
CpFe–C(S)(S)FeCp (**4**), (OC)(CO)(CO)	306.3	d

Table 1 (Cont.)

a. Reference 26.

b. Recorded in THF (-78 °C).

c. Reference 10c.

d. This work.

e. This work, compound prepared according to Angelici's procedure [8c], other absorptions: δ 213.4 (CO), 137.1, 129.9, 129.3, 127.8 (Ph), 88.2 (Cp), 46.8 (CH2).

f. F. B. McCormick and R. J. Angelici, Inorg. Chem., 20 (1981) 111; data in CD_3CN.